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Cite as: AIP Conference Proceedings **1785**, 040093 (2016); https://doi.org/10.1063/1.4967150
Published Online: 18 November 2016

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Abstract. A novel method of creating new lightweight aluminum-metallic composite materials in halide melts at temperatures of 973–1073 K in air atmosphere is proposed. The method for synthesizing aluminum-based metallic composite materials containing up to 2 wt. % graphene sheets uniformly distributed in a metal matrix is entirely new, having no analogies in current science and practice. The synthesis of graphene nanosheets in a metal matrix is a one-step simultaneous process taking place directly in molten aluminum in alkali halide melt without the necessity of a separate stage of synthesis and introduction of graphene. This has the potential to facilitate the inexpensive synthesis of aluminum-graphene composites with a high concentration of graphene. Aluminum-graphene composites formed according to this method are characterized by a high uniformity of graphene films with linear dimensions from 100 nm to 50 μm and a thickness from 1 nm to 3 nm in the metal bulk. No aluminum carbide forms under synthesis; aluminum-graphene and aluminum-graphite composites are resistant to corrosion in a NaCl solution. The hardness, strength and ductility of aluminum-graphene composites are at least 2–3 times as high as the initial aluminum material, proportional to the concentration of graphene.

INTRODUCTION

Research on aluminum metallic composites with carbon content has been done in recent years due to the need of lightweight and resistant alloys in numerous industries, such as automotive, aircraft or battery technology. Traditional methods tend to show poor operational and technological properties caused by the weak wettability of carbon by molten aluminum and a notable density difference between them [1]. The consequence is low resistance to interlayer shift and a tendency to transversal breakage. Corrosion of aluminum-graphite composites is another significant problem. The temperature of the process (up to 1373 K) causes the carbon dissolution and the formation of aluminum carbide. It is completely hydrolyzed in the aqueous media with aluminum hydroxide and gaseous hydrocarbons. Even small aluminum carbide additions damage aluminum-graphene composite materials in aggressive environments, and even in atmospheric conditions. This paper is focused on explaining a new method for aluminum-carbon synthesis with high concentration and uniform distribution of graphene sheets free of aluminum carbide [2]. These metallic composites have a composition of carbon up to 2% in weight and no aluminum carbide formation at 1073 K.

Mechanics, Resource and Diagnostics of Materials and Structures (MRDMS-2016)
AIP Conf. Proc. 1785, 040093-1–040093-5; doi: 10.1063/1.4967150
Published by AIP Publishing. 978-0-7354-1447-1/$30.00

MATERIALS AND METHODS

The interaction between the molten aluminum and the carbon-containing component was performed in molten alkali halide media using an alumina crucible. A disk made of commercial aluminum, 3 cm in diameter and 1 cm high, is used for this method. The sample has 0.65 wt.% of impurities. Salt mixtures of alkali chlorides, such as LiCl, NaCl, KCl, CsCl and $CaCl_2$, with melting points below 700 °C were used as a base electrolyte. Small fluoride additives of NaF or AlF_3 (less than 2 wt.%) formed a part of the salt flux electrolyte. Metal or non-metal carbide powders, such as WC, TiC, ZrC, Mo_2C, SiC or B_4C, were used as a carbon-containing additive. The pre-melted salt electrolyte was fully mixed with a precise amount of carbide powder. This medley was then placed on the bottom of the crucible. Then, the aluminum was loaded into the part of the salt mixture on the bottom, and some medley was also placed on the top of the molten aluminum to prevent its oxidation in contact with oxygen. The temperature interval for the experiments was 973–1073 K. The interaction temperature was chosen under the melting point of both the aluminum (935 K) and the salt mixture. These temperatures are lower than that of aluminum carbide synthesis. The exposure time varied from 0.5 to 5 hours. After high temperature exposure, the liquid aluminum globule is poured into an alumina crucible under controlled cooling. After the salt mixture solidifies, it is dissolved and washed off from the aluminum surface.

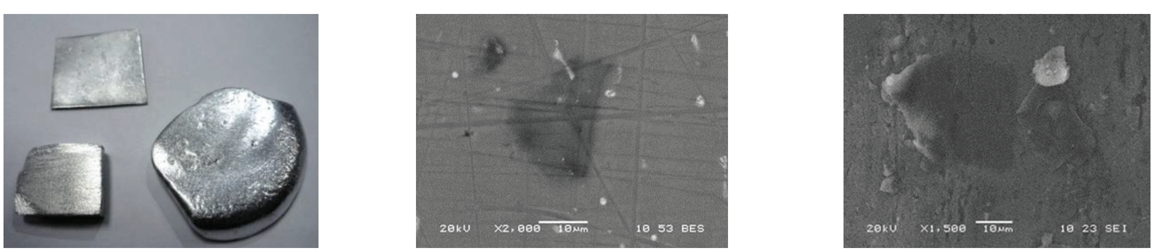
The aluminum-graphene composite samples were cut into two halves. The first half was poured by current-carrying gum and then polished by six different silicon solutions using a Struers disc-finishing machine (Austria). The specimen was then examined as follows: by scanning electron microscopy (SEM) using a JEOL 5900LV microscope; by Raman spectroscopy using a Renishaw-1000 Raman microscope-spectrometer with a green 514 nm argon laser; by an Instron 8801 servohydraulic testing machine; by a Veeko Wyko NT 1100 optic profilometer-profilograph in the Vertical Scanning Interferometry (VSI) regime; by micro hardness testing using a WIN-HCU Fischerscope HM 2000 XYm system designed for Martens test under a load in accordance with the standard ISO 14577. Elastic modulus was determined by unloading curves by the standard Oliver-Pharr method. The Oliver-Pharr method [25] is the most frequently adopted method in instrumented indentation testing to probe the elastic modulus of materials.

Some aluminum-graphene samples were cold-rolled into thin 100 μm foil or 100 μm wire.

RESULTS AND DISCUSSION

It was shown by previous investigations that the direct mixing of carbon micro- and even nanopowders into molten aluminum is impractical because of the extremely poor carbon wettability by liquid aluminum, resulting in composites that are very porous and non-homogeneous. The problem of wettability of carbon particles by molten aluminum can be easily solved by application of molten alkali chloride and sometimes fluoride as reaction media. The ion diffusion coefficients in molten halides are compatible with the diffusion coefficients in molten aluminum. This allows the chemical interaction of carbon-containing substances with liquid aluminum to be carried out with a large yield of aluminum composites with high carbon content at relatively low temperatures in air.

The synthesis of carbon particles inside an the aluminum matrix proceeds by a one-step reaction of carbon-containing components of the molten halide mixture with the molten aluminum, which results in graphene sheets and/or graphite crystals obtained in molten aluminum, which are well wetted by aluminum. Aluminum-graphene composites produced by the proposed method are compact and nonporous, with a characteristic metallic shine (Fig. 1a) and good thermal and electrical conductivity.



(a) (b) (c)

FIGURE 1. A photo of aluminum-graphene composite samples (a), a BES image of polished Al-graphene composite foil (b) and a SEM image of aluminum-graphene wire (c)

The optical and electron microscopy study of the aluminum-graphene wire surface (Fig. 1b) and polished aluminum-graphene foil (Fig. 1c) demonstrates that there are multiple transparent single- or multilayer films. According to the chemical analysis, these films consist of pure carbon. It is obvious that thin graphene films remain on the aluminum-graphene composite surface after rolling into 100 µm foil and subsequent polishing or wire drawing. It is evident that, after the rolling of the aluminum-graphene composite, the concentration of graphene sheets on the metallic surface increases as if the pressure in the rolling extrudes graphene from deeper layers to the surface. Graphene does not form a continuous net through all the aluminum surfaces but represents many separate films.

The phase purity and crystallinity of carbon inclusions was investigated by Raman microspectroscopy due to the sensitivity of the method to the full range of structural states of carbon (diamond, graphite, graphene and others). Fig. 2 illustrates a typical Raman spectrum of transparent carbon film in the aluminum matrix. The dimensions of the graphene sheets are quite significant (25 µm to 35 µm). The Raman spectrum is a typical graphene spectrum. It contains all the characteristic graphene peaks: G at 1578 cm^{-1}, D at 1339 cm^{-1} and 2D at 2674 cm^{-1}. All the peaks are symmetrical and very well defined. The intensity ratio I_{2D}/I_G is equal to 1. This implies the formation of bi-layered graphene [3].

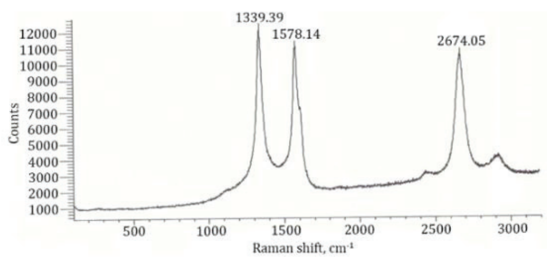


FIGURE 2. The Raman spectrum of thin carbon film on the surface of aluminum foil

2D and 3D images of the aluminum-graphene sample cross-section is shown in Fig. 3. It is obvious that extended graphene film, not connected into the net, forms in the aluminum matrix without formation of any interaction products, such as Al_4C_3. The absence of aluminum carbide formation was confirmed by prolonged corrosion testing in 3% NaCl for 4 months at room temperature. No gaseous products of aluminum carbide hydrolysis were observed. The aluminum-graphene composites were classified as class 4 in characteristic corrosion (durable), whereas basic aluminum is class 3 (quite durable).

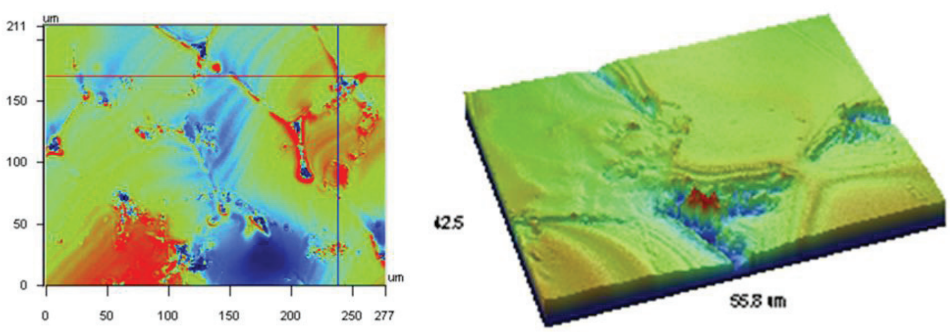


FIGURE 3. 2D and 3D images of graphene films in the aluminum matrix cross-section

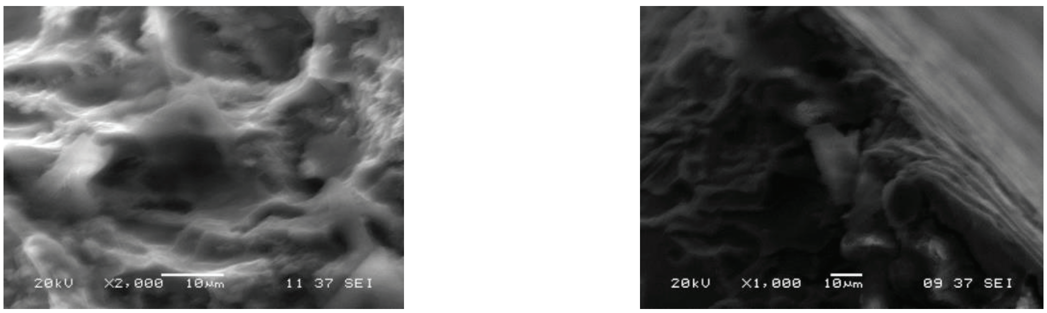
As can be seen in the table of results, hardness increases in aluminum-graphite/graphene composites. In aluminum graphene, the hardness increase is directly proportional to the amount of graphene. This hardness is at least 2–3 times as high as that of the initial aluminum. The Young´s modulus also increases significantly with graphene concentration, whereas it slightly decreases in the aluminum-graphite material.

Figure 4 shows high-magnification scanning electron microscopy images of the fractured surfaces of aluminum-graphene samples with different graphene contents. Although the fractured surfaces of all the Al-graphene samples with different graphene contents exhibit the same plastic strain as the initial aluminum, the smoothness of the fractured surfaces is much different. It is well seen from Fig. 4 that the composite fracture occurs in the metal matrix rather than on the thinnest graphene sheets. It may result from the fact that graphene has the highest fracture toughness of all the materials.

The improvement of hardening according to the elongation of an aluminum-graphene composite is due to graphene, which has high strength and elastic properties. Relative sliding, or delamination, between the graphene layers can also dissipate a part of the fracture energy, leading to an increase in fracture toughness.

TABLE. The properties of aluminum-carbon composites

	Al	**Al–1% graphene**	**Al–2% graphene**
Melting point, K	662 °C	660 °C	658 °C
Specific density, g·cm^{-3}	2.7	2.5	2.4
HV 2000 mH	16.72	45.32	57.19
Elastic modulus, GPa	60.61	82.48	87.93
Tensile strength, R_m, MPa	61.87	80.4	93.78



(a) (b)

FIGURE 4. SEM images of the fractured surfaces of aluminum-graphene samples with 1.0 wt.% (a) and 0.2 wt.% (b) graphene contents

This simultaneous increase in hardness and elastic modulus is very unusual, and it can only be explained by a high concentration of graphene, which simultaneously provides hardness and elasticity.

The addition of graphene into an aluminum matrix increases strength, hardness, ductility and elasticity. For this reason, this application of graphene may be the best strengthening carbon additive for improving the mechanical properties of aluminum. Aluminum-graphene composites can be remelted using conventional methods and rolled into thin foils without the loss of original properties.

CONCLUSIONS

Aluminum-graphene and aluminum-graphite metallic composite materials with uniformly distributed carbon inclusions inside the aluminum matrix have been synthesized for the first time by the chemical interaction of metal or non-metal carbides with molten aluminum in at temperatures ranging between 973 K and 1073 K in air. The thus-obtained metallic composites have specific densities from 2.4 to 2.5 and possess a characteristic metallic shine and electrical conductivity.

The synthesis of aluminum-carbon metallic composites with an improved structure and unique mechanical properties proceeds at relatively low temperatures without aluminum carbide formation; as a consequence, these composites have sufficiently high corrosion resistance. The hardness, strength, ductility and elasticity of aluminum-graphene composites are higher than those of the initial aluminum materials, corresponding to the concentration of graphene.

ACKNOWLEDGMENTS

The tests were performed on the equipment installed at the “Composition of Compounds” Shared Access Centre for Analytical Support and the “Plastometriya” Collective Use Center affiliated to the Institute of Engineering

Science, UB RAS. The study was partially financed by the Russian Foundation for Basic Research (project No. 16-08-01011).

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